BETA-PINENE-OXIDE

AND ITS REACTIONS

By

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INTRODUCTION

The principal purposes of the research covered by this thesis were the preparation of beta-pinene-oxide from beta-pinene and to conduct exploratory studies of possible new syntheses involving beta-pinene-oxide.

The products were identified by means of melting points, boiling points and refractive indices. No attempt was made to identify any of the by-products of the reactions. It was assumed that products in the higher boiling fractions were polymerization products of beta-pinene.

Purified beta-pinene was used in this work. The technical grade beta-pinene, purchased from Arizona Chemical Company, was distilled. The fraction boiling at 163-165°C was used throughout the experiments.

HISTORICAL

Occurrence

Beta-pinene occurs in nature in the majority of the oils in which alpha-pinene is found. The percentage present is variable, and as a rule is considerably lower that alpha-pinene. The constitution of beta-pinene was established by oxidation of l-nopinic acid. (44,38,26, 61,62,63,22,13,23,21)

Reactions of Beta-Pinene

In general the reactions of beta-pinene resemble very closely those of alpha-pinene, but investigation was hampered by the difficulty of effecting a complete separation of the two hydrocarbons. Austerweil (2) suggested taking advantage of the greater solubility of beta-pinene in alcohol. In 72 percent alcohol, alpha-pinene has a solubility of 2 percent and beta-pinene of 9 percent, while in 65 percent alcohol at 15°C it is 0.6 and 3.3 percent respectively. Further difficulties in investigating the reactions of beta-pinene lay in the great tendency which it showed to isomerize into the alpha-pinene (3). It has been shown that when it was heated with rosin at 160°C for twenty hours, over seventy percent is isomerized to alpha-pinene. When beta-pinene was heated under pressure at 270°, polymerization to a diterpene occurred. This product had a boiling point 170-185°C/10 mm. (48)(49)

Hydrogenation

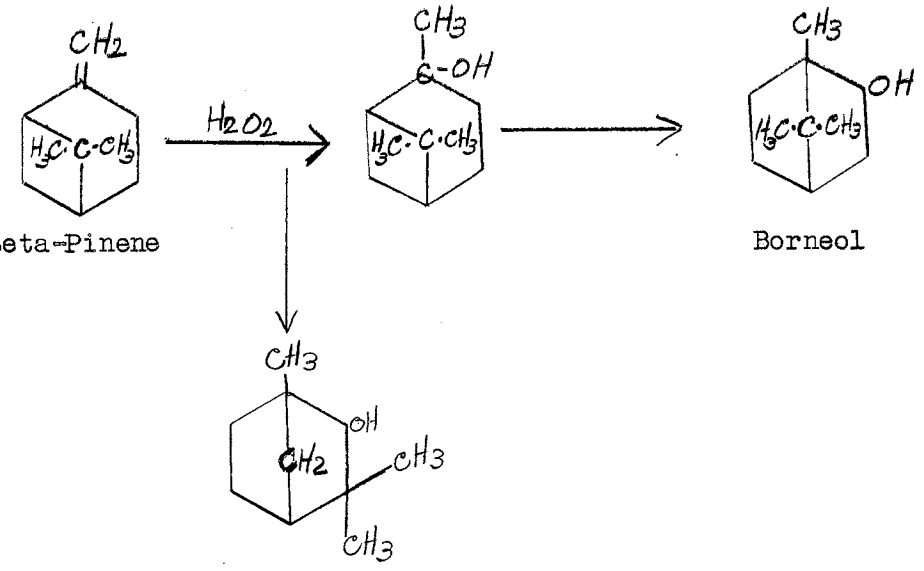
On catalytic hydrogenation (59) beta-pinene behaves like alpha-pinene and yields pinane.

Autoxidation

On autoxidation in the presence of catalysts beta-pinene yielded a mixture of d-pinocarveol, l-myrtenol and l-myrtenal. (47) Oxidation with selenium dioxide gave d-pinocarveol, d-pinocarvone and l-myrtenal. (53)(54)

Oxidation with Ozone and Hydrogen Peroxide

The oxidation of beta-pinene with ozone was investigated by Brus and Peyresblaugues and others. (18) (16) (46). The ozonolysis proceeded smoothly and in the manner anticipated yielding formaldehyde and nopinone in a yield of approximately fifty percent. A small quantity of a lacton, $C_9H_{14}O_2$, was also formed. Henderson and Chisholm (30) examined the products which were formed when beta-pinene was oxidized with hydrogen peroxide. The oxidation proceeded in a somewhat different manner to that of alpha-pinene, yielding a mixture of borneol and fenchyl alcohol; therefore, hydrogen peroxide acted as a hydrating agent since both borneol and fenchyl alcohol result from the hydration of oil of turpentine. (8)



Beta-Pinene

Borneol

Fenchyl Alcohol

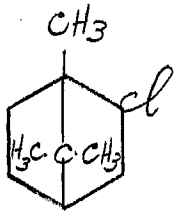
Oxidation with Permanganate

By oxidation of beta-pinene with potassium permanganate l-nopinic acid was formed. (15)(65) Chromyl chloride reacted with beta-pinene, yielding an addition compound $C_{10}H_{16}$, 2 Cr O_2Cl_2 which was decomposed by water yielding a lacton and mixture of aldehydes and dl-trans pinoglycol. (30)

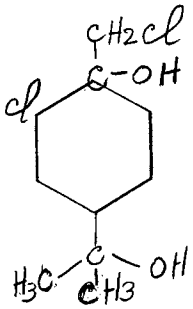
Halogens and Hydrogen Chloride

Chlorine reacts with beta-pinene at 15°C to 20°C for four hours with the formation of bornyl chloride and oily fractions of di and tri chloro derivatives. Bromine reacts with beta-pinene in carbon tetrachloride with a similar result. (17)

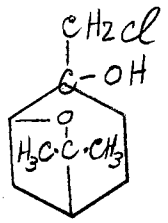
Formation of bornyl chloride from beta-pinene involved the isomerization of beta-pinene to alpha-pinene. Wagner (60) recognized that a molecular rearrangement was involved in the formation of bornyl chloride from alpha-pinene. (35)(33)



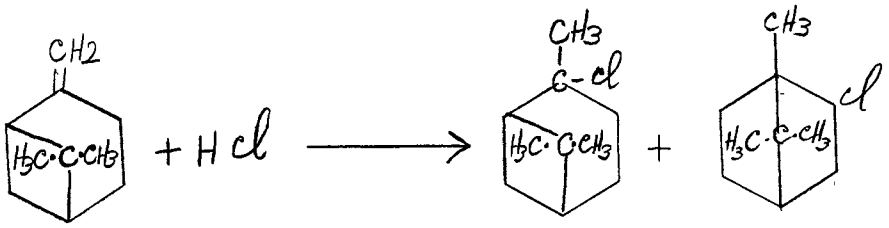
With hypochlorous acid beta-pinene reacted in a similar manner to alpha-pinene. Henderson and Kerr (31) have prepared by the action of this reagent, three crystalling dichlorohydrins, which were probably dichloro-p-methanediols. They melted at 135°C, 166°C and 131°C respectively. Owing to the poor yield and the difficulty of separating these isomerides, it has not proved possible to determine their constitution. The dichlorohydrin, m.p. = 135°C was represented by



since both the hydroxy groups appeared to be tertiary, and on treatment with alkali yielded a monochlorohydrin m.p. = 125°C, probably with the structure represented by



since it was not identical with pinol monochlorohydrin. Hydrogen chloride yielded pinene hydrochloride and bornyl chloride upon reaction with beta-pinene. (1)



Pinene-Hydrochloride Bornyl Chloride

Hydration

Considerable attention has been devoted to the subject of hydration of beta-pinene, and there has been much discussion, especially among the French workers, as to whether alpha and beta-pinene behaved similarly on treatment with hydrating agents like dilute mineral acids and organic acid. Alpha-pinene yielded a mixture of monocyclic terpenes, alpha-terpinol, borneol and fenchyl alcohol. It was suggested that the

dicyclic alcohols were formed in greater amount from beta-pinene. The experiments done by Austerweil and his collaborators (4)(5), using benzoic acid as hydrating agent, have led to the conclusions that in all cases of hydration, beta-pinene was partially converted into alpha-pinene, and that the hydration of alpha and beta-pinenes gave products which were qualitatively the same, but quantitatively different. With beta-pinene the dicyclic alcohols, borneol, isoborneol and fenchyl alcohol were the main products. This factor was one of considerable technical importance in view of the use of isoborneol for the preparation of synthetic camphor.

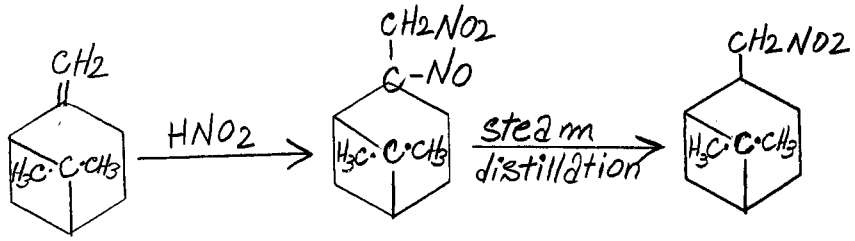
While dilute mineral acids hydrated beta-pinene, Brooks and Humphery (14) have shown that with concentrated sulfuric acid at 0°C, polymerization occurred with the formation of hydrocarbons of the composition $C_{20}H_{32}$ and $C_{30}H_{48}$.

In connection with hydration of beta-pinene Delephine and Adida (19) have found that with picric acid beta-pinene reacted in exactly the same way as alpha-pinene, yielding bornyl and fenchyl picrates.

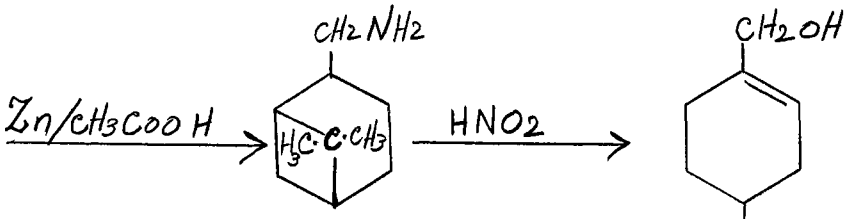
Action of Nitrous Acid

Wallach and Isaac (66) studied the reaction of beta-pinene with nitrous acid. They obtained nitropinene. This compound, on reduction with zinc dust in acetic acid solution, gave an amine aminopinene b.p = 95°/12 mm, $d^{19°} = 0.9325$, $n_D^{19°} = 1.4960$. The aminopinene was very unstable and yielded, with nitrous acid, the monocyclic alcohol. This alcohol, upon oxidation with chromic acid, gave a mixture of cuminaldehyde and cumic acid.

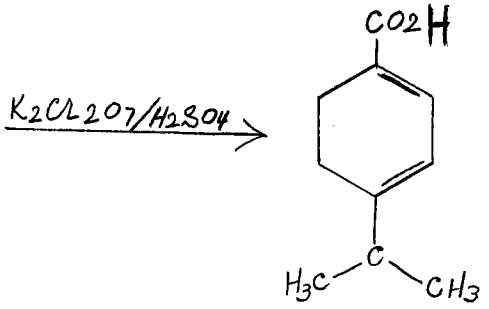
Although the constitutions of nitropinene and its derivatives have not been rigidly proved, there would appear to be little doubt that the reactions oulined above proceed in accordance with the following scheme:



Beta-Pinene Beta-Pinene-Nitrosite Nitropinene



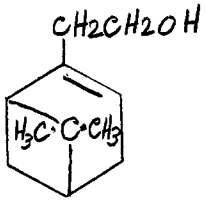
Aminopinene



Cumic Acid

Condensation

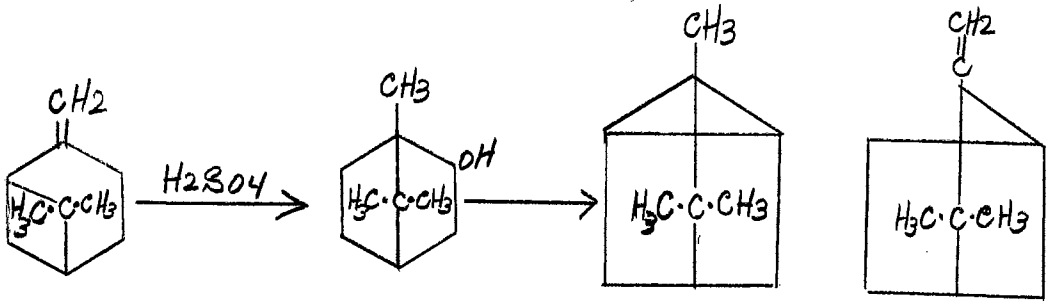
Beta-pinene condenses with formaldehyde to give the alcohol (nopol) (7) b.p = 110.5°/10 mm, $d_4^{25°} = 0.9647$, $n_D^{25°} = 36.5°$ the formation of this alcohol involves a migration of the ethylenic linkage into the ring



Nopinol

Molecular Rearrangement

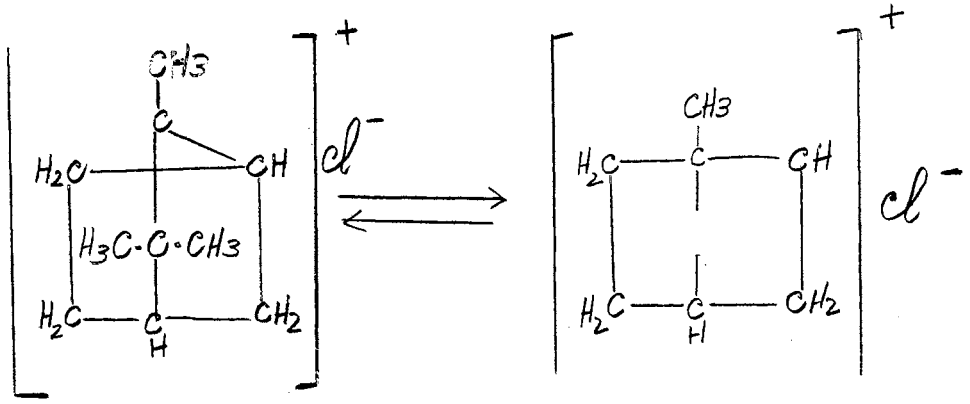
The hydration of alpha and beta-pinene yielded isoborneol and fenchyl alcohol, and also the dehydration of isoborneol to camphene. For instance, in the conversion of isoborneol into camphane it has been assumed that tricyclene was an intermediate product. (34)



Beta-Pinene Isoborneol Intermediate Camphene

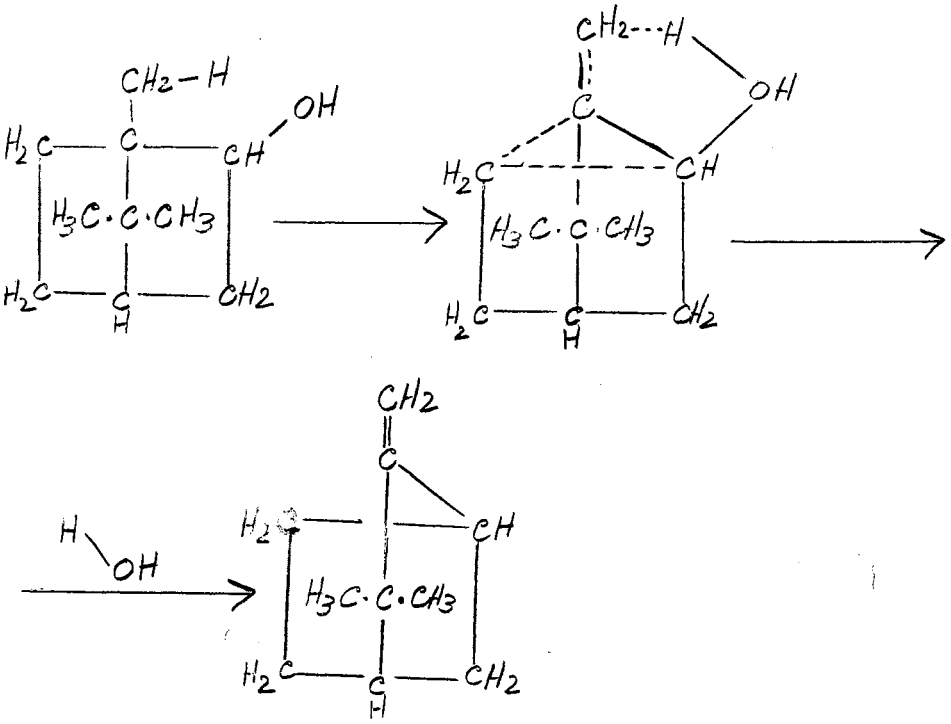
Further evidence was furnished by a study of the velocity of the conversion of camphene and tricyclene into isobornyl chloroacetate by the action of chloroacetic acid. The esterification of camphene proceeded with a far greater velocity than that of tricyclene, which could obviously not be the case if tricyclene was an intermediate stage in the reaction.

Meerwein (34) considered that the isomerization was preceded by ionization, the actual molecular rearrangement occurring in the cation. Evidences in support of this view were afforded by a study of the velocity of the change of camphene hydrochloride to isobornyl chloride (35)(36)

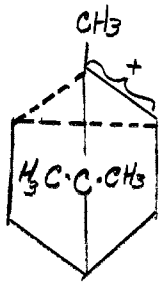


Camphene Hydrochloride Isobornylchloride

Robinson (42), in his precise and adequate method, expressed correlation of these changes with the pinacolin transformation.



Ingold(32) has suggested that an intermediate ion in the camphene borneol change can be regarded as the modern equivalent of the partial valency formula. (39)



Epoxidation

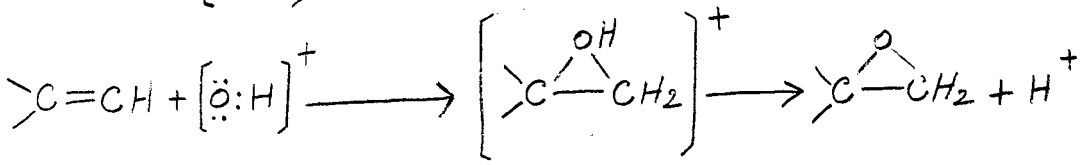
Oxiran (alpha-epoxy compounds) can be prepared from olefins by a variety of methods. One of the most important and most generally applicable of these methods is oxidation of ethylenic compounds with organic peracids (57)(58)(55). One of the pioneers in this field is the Russian chemist Prileschajew (40) who showed that perbenzoic acid is an efficient oxidizing agent for the epoxidation of isolated double bonds.

$$-\overset{|}{C}=\overset{|}{C}- + C_6H_5CO_3H \xrightarrow[\text{solvent}]{\text{organic}} -\overset{|}{C}-\overset{|}{C}- + C_6H_5CO_2H$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad O$$

Some investigators have treated solutions of benzaldehyde and the unsaturated compound with air or oxygen, the perbenzoic acid being consumed as it was formed. Other organic peroxyacids like peracetic acid (28), monoperphetalic acid (12), and percamphoric acid (37) also have been used for the purpose of epoxidation.

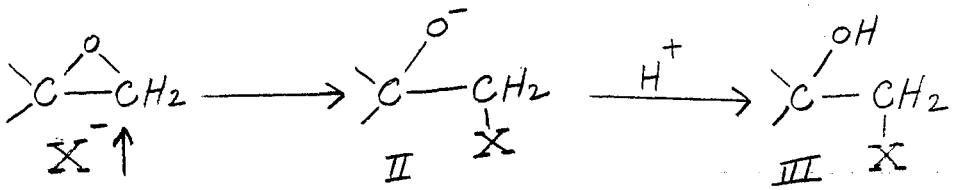
Mechanism

It is evident from the numerous reactions that organic peracids are electrophilic reagents.(56) It is proposed that the attacking moiety in peracid oxidations is the electropositive polarized (electrophilic) hydroxyl group $\left[\ddot{O}:H\right]^{+}$ (67)(43). A reasonable mechanism involves essentially direct formation of conjugate acid of the oxirane by donation of $\left[\ddot{O}:H\right]^{+}$ to the olefin by a peracid.

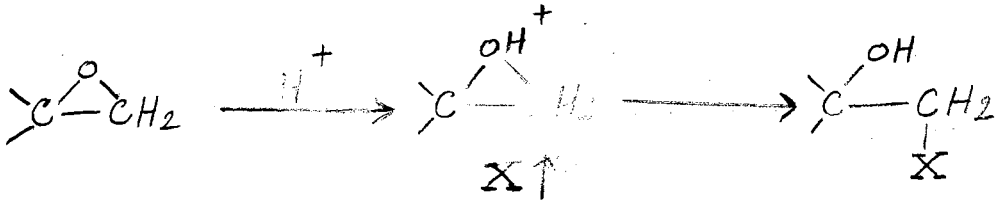


Mechanism of Epoxide Reaction

The reactions of epoxides invariably involve the opening of the oxide ring. The mechanism by which this occurs is a nucleophilic displacement on carbon, with the ring oxygen atom as the displaced group. (24) Such a displacement is illustrated below



Displacement on the oxide itself gives II as the intermediate which, upon acquiring a proton, gives III as the final product. The displacement may also take place on the much more reactive conjugate acid of the oxide as illustrated by the following equation.



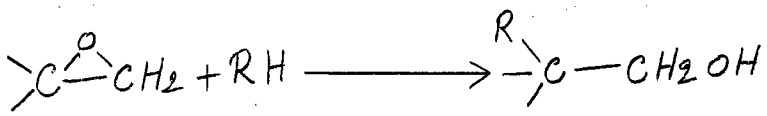
As the consequence of the ready attack on the conjugate acid of the oxide, acid catalysis of the reactions of the oxide is very common.

If the attacking nucleophilic agent symbolized by YH is capable of reacting with a base B^- so as to convert at least part of YH to a more strongly nucleophilic agent Y^-, then the attack on epoxide will be carried out by Y^-. An equation for the formation of Y^- by the reaction of YH with base B^- is shown below

$$YH + B^- \longrightarrow BH + Y^-$$

It is in this manner that the observed base-catalyzed reactions of epoxide can be explained.

The reactions of epoxides can be divided into two classes. The first of these encompasses the active hydrogen compounds.



The other class involves the reaction of compounds not containing active hydrogen.

A comprehensive survey and bibliography of epoxide literature has been made by Dure.(20)

EXPERIMENTAL - PART A

Preparation of Beta-Pinene Oxide

Peracetic Acid

Thirty-nine and five-tenths grams (0.29 mole) of distilled beta-pinene, B.P = 163-164°C, $[\alpha]_D = -22.44$, $n^{15} = 1.4872$, was placed in a three-necked flask equipped with a reflux condenser, a thermometer, and a mechanical stirrer. After this, 2.8 grams of anhydrous sodium acetate was added to the beta-pinene. Then 57.3 grams (0.302 mole) of Becco peracetic acid 40% (9)(10)(11) was slowly added over one hour at a controlled temperature of 20°-25°C.

Approximately one-third of the peracid was added during the first half hour, while the balance was added over the second half hour. During the peracid addition, a temperature response was observed after each increment had been added. The reaction was continuously stirred at 25°C. After two hours, titration of an aliquot of the mixture (29) (52) showed that 60% of peracetic acid had been consumed. After this period the mixture was warmed to 50-60°C and held at that temperature for one hour. The product was isolated by transferring the reaction mixture to a separatory funnel, drawing off the lower aqueous layer, and washing the oil layer with warm water (50-60°C) until free of acid. The oil was dried with a minimum amount of anhydrous magnesium sulfate and filtered. The product was distilled at 30 millimeters pressure. The boiling point was found to be 71-72° which checked with

the boiling point of pure beta-pinene at the same pressure.

Duplicate results were obtained with different temperatures, time and molar concentrations. It was concluded that Becco peracetic acid did not epoxidize the beta-pinene.

Preparation of Perbenzoic Acid

Five grams of metallic sodium was placed in a 500 milliliter conical flask provided with a reflux condenser and then 100 milliliters of absolute methyl alcohol was added to the flask. The resulting solution of sodium methoxide was cooled to -5° in a freezing mixture of ice and salt. Then the condenser was removed and fifty grams of freshly recrystallized benzoyl peroxide (27) in two hundred milliliters of chloroform was added with shaking and cooling at such a rate that the temperature did not rise above 0°. The mixture was kept in the ice-salt bath for five minutes with continuous shaking. The solution turned milky, but no precipitate appeared. The mixture was transferred to a one-liter separatory funnel and the sodium perbenzoate was extracted with five hundred milliliters of water containing much crushed ice. The chloroform layer was separated and aqueous layer was extracted twice with one hundred milliliter portions of cold chloroform to remove the methyl benzoate. Perbenzoic acid was liberated from aqueous solution by the addition of 225 ml. of ice-cold one normal sulfuric acid, and the product was extracted from solution with three 100 ml. portions of cold chloroform. The chloroform solution was dried with anhydrous sodium sulfate.

Perbenzoic acid in ether solution was obtained by drying the above chloroform solution for an hour with sodium sulphate, and

chloroform was removed under reduced pressure at ordinary temperature while carbon dioxide was introduced through a capillary tube. The white to pale yellow residue was dried for ten hours at 30-35° under 10 mm. pressure and was kept in a dark, cool place. The material had a melting point of 42°. These crystals were dissolved in an anhydrous ether solution.

Preparation of Beta-Pinene-Oxide by Perbenzoic Acid

In a three-necked flask, equipped with a thermometer, a reflux condenser and a mechanical stirrer, was placed 39.5 grams (0.29 mole) of beta-pinene. Then 42 grams (0.30 mole) of perbenzoic acid in 500 milliliters of chloroform was added over a period of one hour. The mixture was continuously stirred at 0°C. Periodic acid titration (29) of the mixture showed that after 35 hours a slight excess of perbenzoid acid remained in the solution.

An oily layer was separated after adding dilute solution of sodium hydroxide. The product was washed three times with dilute sodium hydroxide. It was then dried by a minimum amount of magnesium sulfate. Fractional distillation of the liquid gave a 61-63% yield. The physical constants of the liquid was

Boiling Point	80-82°C/10 mm.	
Refractive index	$n_D^{18} = 1.4790$	
Density	$d_4^{18} = 0.9756$	
Specific rotation	$[\alpha]_D = +7.75$	(10% $CuCl_2$)

Further preparation of beta-pinene-oxide was done by the following method. This time the same procedure was used, but with ether in place of the chloroform as a solvent. The mixture was continuously stirred at room temperature, and the time required for completion of reaction was 24 hours. After fractional distillation, the resulting compound had the same physical constants as before, but the yield was 85%.

EXPERIMENTAL - PART B

Reaction of Beta-Pinene-Oxide with Lithium Aluminum Hydride

Introduction

Lithium aluminum hydride, one of the group of complex metal hydrides, is a useful and convenient reagent for the selective reduction of various polar functional groups. Nearly all the normal reduction reactions involve the displacement of a strongly electronegative atom "oxygen" and accession of a hydrogen atom to the electron deficient center, usually a carbon atom. So the reductive cleavage of epoxide rings is a useful synthetic procedure for introducing a hydroxyl group at the former site of a double bond. A secondary oxide linkage is attached in preference to a tertiary, and the normal product from such a combination is a tertiary alcohol, with the consideration that there are some exceptions. With the above details it is a reasonable procedure to prepare methylnopinol by action of lithium aluminum hydride on beta-pinene-oxide.

Procedure and Results

Fifteen grams (about 0.4 mole) of lithium aluminum hydride in two hundred milliliters of ether was placed in a three-necked flask equipped with a mechanical stirrer and a condenser (the condenser was equipped with the tube of calcium chloride). The mixture was stirred for a few minutes. Then about 0.2 mole of beta-pinene-oxide in three hundred milliliters of ether was added very slowly from a dropping funnel, while the mixture was being stirred. After all the pinene-oxide was added, the mixture was refluxed for three hours. The calcium chloride was removed and eighty milliliters of distilled water was added very slowly until there was no evolution of hydrogen gas. Ammonium chloride also was added to hydrolyze the remainder of the lithium aluminum hydride. After twenty minutes the mixture was transferred into a separatory funnel, and the ether layer was separated and washed with sodium bicarbonate. The ether was removed by distillation. The solid product was dried and the physical constants of the compound were found to be

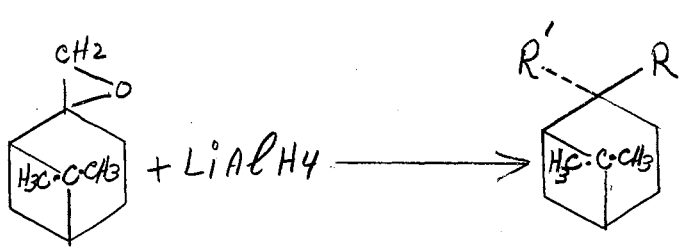
Boiling Point	= 189-190°C
Refractive index	= -24.5 ($CHCl_3$)
M.P.	= 78-80°C
Infrared Spectra	= γ (OH) 3340 cm^{-1}
Formula	= $C_{10}H_{18}O$
Odor	= Camphor

Easily sublimable as needles.

Upon reaction of above compound with five percent sulfuric acid, a solid was obtained with a melting point of 115°C. The compound corresponded to terpin hydrate. The experiment was repeated with alpha-pinene-oxide, but no reaction was observed even after ten hours. The alpha-pinene-oxide was recovered.

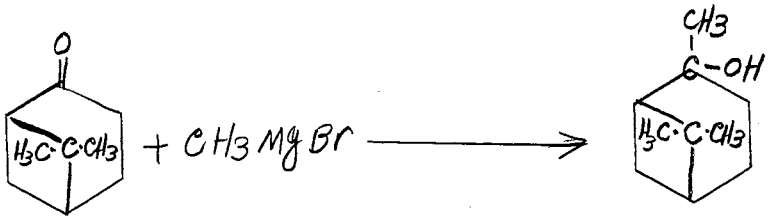
Discussion

It was known that the reduction of an assymetric epoxide with lithium aluminum hydride furnished two possible alcohols, trans and cis. Therefore, it was expected that two isomers would be obtained in the foregoing experiment with beta-pinene-oxide.



	R	R'
a:	OH	CH_3
b:	CH_3	OH

From the investigations of Auwers (6) and Skita (50) it was known that cis and trans forms of a substance differ in density and refractive index. Wallach (61) prepared methylnopinol by reacting methylmagnesium iodide on nopinone.



He assigned the cis configuration (hydroxyl is para in position to dimethyl). The compound which he prepared had the physical constants

M.P.	= 58-59°C
Boiling Point	= 204-205°C
$[\alpha]_D^{20}$	= -4.99

Another attempt was made to prepare methylnopinol by action of potassium permanganate on pinane. A compound with the melting point of 79°C was formed. Upon reacting the compound from the oxidation with five percent sulfuric acid only terpen hydrate was obtained.

By the comparison of the melting points of these three methylnopinols it was observed that the melting point of methylnopinol obtained by reaction of lithium aluminum hydride was very close to the melting point of methylnopinol obtained by reaction of pinane with potassium permanganate. Therefore it was assumed that the product of reaction of lithium aluminum hydride with beta-pinene-oxide is trans-methylnopinol. Also it was assumed that inability of alpha-pinene oxide to react with lithium aluminum hydride probably resulted from the effect of steric hindrance of methyl "8" on the epoxide in alpha-pinene-oxide.

EXPERIMENTAL - PART C

Reaction of Beta-Pinene-Oxide with Ethylmagneisum Iodide

Procedure and Results

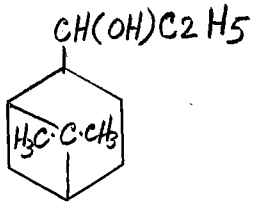
Preparation of Grignard Reagent

Twenty-four grams (one mole) of magnesium turnings and a crystal of iodine were placed in a dry, two-liter, three-necked round bottomed flask fitted with a glycerine-sealed stirrer, reflux condenser, and dropping funnel. The flask was heated until the iodine vaporized. It was allowed to cool while one mole of ethyl iodide was weighed out. Two milliliters of halide was added to the reaction flask, and the remainder was mixed with two hundred milliliters of anhydrous ether. After starting the reaction with a few milliliters of anhydrous ether, an additional fifty milliliters of ether was placed in the flask, and the ether solution of ethyl iodide was added through the dropping funnel at such a rate as to cause gentle refluxing. After the addition was complete, the mixture was stirred for two hours and allowed to stand over night.

Reaction of Grignard Reagent with Beta-Pinene-Oxide

The Grignard reagent, prepared as above, was cooled in an ice-salt bath. One hundred milliliters of anhydrous ether was cooled to 0° and placed in a dropping funnel with a tight cork. One mole (152 grams) of beta-pinene-oxide was measured out in a flask, previously

calibrated and cooled to 0°. The cooled beta-pinene-oxide was mixed with the ether in the dropping funnel and added cautiously to the Grignard reagent. As soon as addition was complete, the ice-salt bath was removed and the mixture was allowed to come to room temperature while being stirred vigorously. The condenser was set for distillation and the flask was placed in a water bath at 70° until about two hundred milliliters of ether had been removed. The condenser was again set for refluxing and two hundred and fifty milliliters of anhydrous benzene was added. Gentle refluxing on the water bath was continued for six hours. Then the mixture was allowed to stand over night. After hydrolysis with one hundred milliliters of distilled water, the benzene layer was decanted. The magnesium hydroxide residue was extracted three times with small portions of ether. The ether and benzene extracts were combined and these extracts were steam distilled from 30% potassium hydroxide solution. This separated the alcohol from the resin that was formed in the experiment. Then the alcohol was dried over anhydrous sodium sulfate and fractionated. The product had the following physical constants: B.P. = 123-125°/10 mm. and $d^{20} = 0.9782$, $n = 1.4892$. The formula for the compound was believed to be



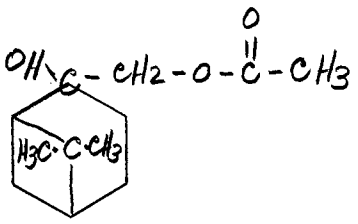
The presence of a secondary alcohol in the above product was shown by a test with hydrochloric acid saturated with zinc chloride. An oily layer was produced in thirty minutes when one milliliter of the product was treated with eight milliliters of hydrochloric acid-zinc-chloride mixture.

EXPERIMENTAL - PART D

Reaction of Beta-Pinene-Oxide with "Acetic Acid"

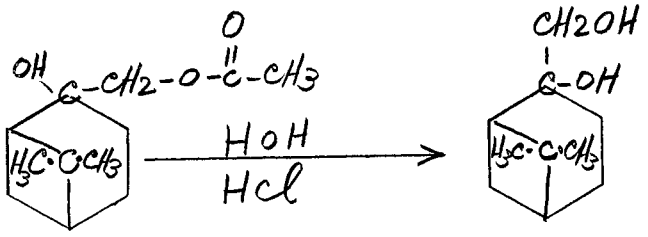
Procedure and Results

Thirty grams (0.2 moles) of beta-pinene-oxide was placed in a dry one-liter, three-necked flask equipped with a mechanical stirrer and a dropping funnel. Fourteen grams of glacial acetic acid was added from dropping funnel over a period of half an hour. The system was kept at room temperature for three days. Distillation gave acetic acid and two fractions with a boiling point of (a) 103°/10 mm., and (b) 153°/10 mm. The formula of the product (b) was proposed as



The boiling point and density of part (a) matched that of fenchyl alcohol.(25)(41) Part (a) was oxidized with chromic acid. The product had a boiling point of 191-193°C, a refractive index of $n^{20} = 1.4635$, and a density of $d^{20} = 0.9480$ which corresponded to fenchone. Part (b) was hydrolyzed with 18% hydrochloric acid and

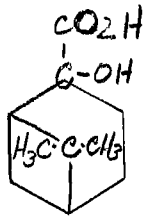
the product obtained had a melting point of 76-78°. The hydrolysis was represented as follows



Beta-Pinene-Glycol

Discussion

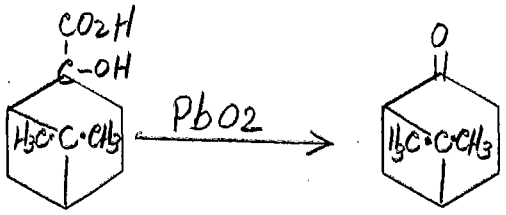
This alcohol was made by Wagner and Brus by oxidation of oil of turpentine. Its derivation from beta-pinene was subsequently established by Wallach (63). When it was warmed with dilute acids it gave a mixture of pinol and an aldehyde. The melting point of the product obtained as (b) above was the same as the beta-pinene-glycol obtained by Wagner. The oxidation of the beta-pinene glycol part (b) with alkaline potassium permanganate gave an acid that had a melting point of 125-127°C with the formula



Nopinic Acid

or nopinic acid. This melting point matched the melting point of nopinic acid obtained by Brus (15) by oxidation of beta-pinene with potassium permanganate.

The treatment of the acid obtained from the permanganate oxidation with lead peroxide produced nopinone.



with a boiling point of 85-87°C/14 mm., and $n_D^{20} = 1.4787$.

Preparation of Nopinone

Two grams of nopinic acid was placed in a flask equipped with condenser and thermometer. A small amount of water was added until it covered the nopinic acid. Then eight grams of lead dioxide was added. The current of steam was passed through the liquid. During the reaction carbon dioxide was evolved and an oily, fresh smelling liquid was obtained in receiving flask. The oily layer was extracted with ether.

The obtained product did not react with potassium permanganate; therefore it was shown not to be an aldehyde. Nor did it have a double bond, so the compound was believed to be a ketone. The structure could be identified through its formation.

DISCUSSION

Beta-pinene and 40% Becco-peracetic acid failed to produce beta-pinene-oxide. It was assumed that the presence of sulfuric acid in 40% Becco peracetic acid prevented the formation of beta-pinene-oxide. Beta-pinene-oxide was obtained by action of perbenzoic acid on beta-pinene.

The yield of beta-pinene-oxide was increased when anhydrous ether was used instead of chloroform as a solvent.

In the reaction of beta-pinene-oxide with lithium aluminum hydride the compound obtained was trans-methyl nopinol.

Alpha-pinene-oxide failed to react with lithium aluminum hydride. It was assumed that probably the effect of steric hindrance of methyl "8" on epoxide was the cause. This was in contrast to the behavior of beta-pinene-oxide.

The Grignard reagent produced a secondary alcohol upon reaction with beta-pinene-oxide.

In reaction of glacial acetic acid with beta-pinene-oxide it was proved that the formation of and the hydrolysis of the acetate proceeded without a shift of pinene structure.

CONCLUSION

1. Beta-pinene-oxide was prepared for the first time in good yield by using perbenzoic acid in ether solution.

2. Beta-pinene failed to react with peracetic acid (40% Becco peracetic acid purchased from Becco Chemical Company) to produce beta-pinene-oxide. Meanwhile the alpha-pinene-oxide was made by Becco Chemical Company with the 40% Becco peracetic acid. This was a departure from the behavior of the two compounds.

3. The reactions of beta-pinene-oxide were different from those of alpha-pinene-oxide in the case of lithium aluminum hydride, and the glacial acetic acid.

4. The reactions of the beta-pinene-oxide showed that it did not isomerize to camphane structure. This was in contrast to many other reactions using beta-pinene.

5. New syntheses for a number of derivatives of beta-pinene are now possible through the use of the beta-pinene-oxide.

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